



A working methodology for the total water determination in inulin by the volumetric Karl Fischer titration

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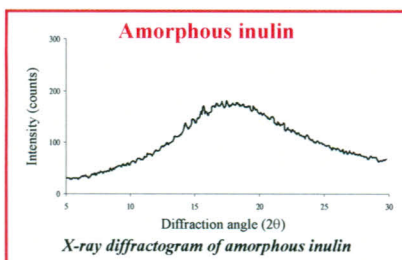


Introduction

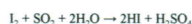
In general, water content is determined by oven drying and does not correctly represent the water content of a sample. Indeed, high temperatures can induce the formation and the release of volatile substances (water and others), while water included in the crystals might not be completely detected. Moreover, due to the rapid adsorption of water on anhydrous material after oven drying, this technique presents poor reproducibility. The Karl Fischer (KF) titration is a well-established method for the water content determination. This technique allows the determination of the total water of a sample and is now the most important primary method for determining water content in foodstuffs. To determine the water content of a sample, it must be dissolved in the reaction medium, used as solvent. In some cases, the medium does not completely dissolve the sample. In order to increase solubility, some authors used an internal homogeniser, worked at elevated temperatures or modified the polarity of the working medium by adding further solvents to it. These methodologies using the KF titration present some inconveniences as not all titration devices are equipped with an internal homogeniser or a heatable titration vessel which limits the use of these techniques for wider applications. More so, at high temperature, possible evaporation of sulphur dioxide from the boiling working medium makes a reflux condenser necessary. For these reason, we developed a suitable sample preparation for the total determination of water content and applied it to inulin, a selected dietary fibre. Inulin samples were analysed by KF titration using the usual method of introducing the powder directly in the methanol base working medium, modified or not by formamide (1:3, v/v) in order to increase sample solubility. In addition, an alternative methodology based on the introduction of an inulin solution in pure formamide was developed and compared to the standard KF titration. These methodologies were applied to two inulin sample which presented either an amorphous or a crystalline state.

Experimentation and results

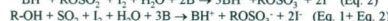
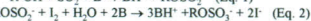
Inulins were stored over P_2O_5 for three weeks at 20°C to obtain a dehydrated product, then analyzed by Powder X-ray diffraction.



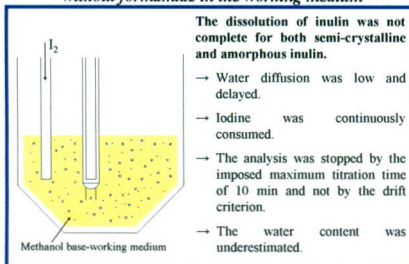
The determination of the water content is based on the reaction described by R.W. Bunsen in 1853:



Karl Fischer discovered that this reaction could be used for water determination by a two-step reaction:



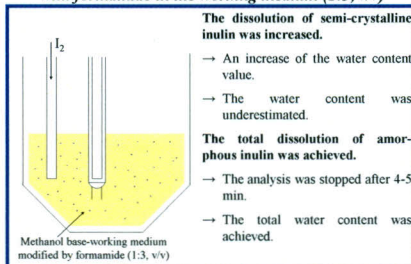
Analysis of powdered inulin by Karl Fischer titration without formamide in the working medium



The dissolution of inulin was not complete for both semi-crystalline and amorphous inulin.

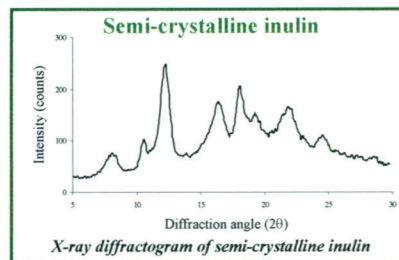
- Water diffusion was low and delayed.
- Iodine was continuously consumed.
- The analysis was stopped by the imposed maximum titration time of 10 min and not by the drift criterion.
- The water content was underestimated.

Analysis of powdered inulin by Karl Fischer titration with formamide in the working medium (1:3, v/v)



The dissolution of semi-crystalline inulin was increased.

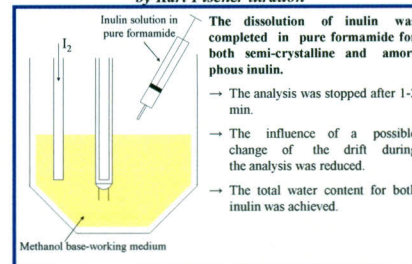
- An increase of the water content value.
- The water content was underestimated.
- The total dissolution of amorphous inulin was achieved.
- The analysis was stopped after 4-5 min.
- The total water content was achieved.



An iodine molecule is attracted to the negatively charged platinum pin. It then acquires two electrons and turns to iodide ($2I^-$). The two negatively charged iodide ions are immediately attracted to the positively charged platinum pin, where they donate the electrons and form an iodine molecule again.

When the reagent consumption rate reaches the same (or a slightly higher) value as immediately before the start of the analysis, it is assumed that all the water of the sample is detected, and the analysis is stopped. If the sample is not completely dissolved, water diffusion is low, so the analysis is delayed and underestimated.

Analysis of inulin dissolved in formamide (2.5:7.5, w/w) by Karl Fischer titration



The dissolution of inulin was completed in pure formamide for both semi-crystalline and amorphous inulin.

- The analysis was stopped after 1-2 min.
- The influence of a possible change of the drift during the analysis was reduced.
- The total water content for both inulin was achieved.

Conventional KF method without formamide	Conventional KF method with formamide	Proposed KF method
1.3 ± 0.3 (>10min)	2.1 ± 0.1 (4-5min)	2.1 ± 0.2 (1-2min)
1.1 ± 0.3 (>10min)	1.8 ± 0.3 (>10min)	2.4 ± 0.1 (1-2min)

Results of the Volumetric Karl Fischer titration (g water / 100 g anhydrous sample) (Amorphous inulin, Semi-crystalline inulin)

Conclusions

The total water content of inulin has been determined by volumetric Karl Fischer titration, using a complete pre-dissolution of the sample in pure formamide, and was compared to the usual introduction of the sample directly in the methanol-based working medium, modified or not by addition of formamide (1:3, v/v) in order to increase sample solubility. The described method allowed the determination of water included in the crystals, as shown by comparing the results for amorphous and semi-crystalline inulin samples.

The titration time for the proposed method was 1 - 2 min, while complete water detection was not achieved after 10 min by the standard method. Dissolving the sample beforehand and transferring an aliquot into the titration cell is time consuming, but this is compensated by the shorter titration time. This advantage is even more important, when routine analyses are carried out and several samples can be dissolved simultaneously. Moreover, the proposed method has the advantage of working at ambient temperature and can be applied to every volumetric KF titrator. This methodology can be applied for the water content determination of other polysaccharides presenting a solubility problem in the working medium.

Acknowledgments

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Reference: S. N. Ronkart, M. Paquot, C. Fougnyes, C. Deroanne, J.-C. Van Herck, C. Blecker. (2006). Determination of total water content in inulin using the volumetric Karl Fischer titration. Talanta, 70, 1006-1010.

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The aim of this research work was to quantify total water in inulin by Volumetric Karl Fischer Titration. This polysaccharide presents a solubility problem in the methanol working medium (MWM), even when the polarity of the system is increased by addition of formamide. So, when using the conventional Karl Fischer method, water diffusion of the sample is low, and the measure is stopped by the length of the analysis and not by the stabilization of the drift.

By externally dissolving inulin in formamide (2.5:7.5, w/w) and injecting this solution into the MWM, total water including crystallization water, is successfully extracted and quantified. The developed method was compared to the usual Volumetric Karl Fischer Titration method of introducing the sample directly in the MWM, modified or not by formamide (1/3, v/v).

Amorphous inulin analysed with the developed method lead to the same water content determination as the introduction of inulin powder in the titration cell with addition of formamide (2.07 g water/100 g anhydrous inulin), but the analysis time is reduced by at least a factor 2. However, the water content of semi-crystalline inulin is higher than that analysed by the introduction of inulin powder in the titration cell (2.35 instead of 1.10 g water/100 g anhydrous inulin). This difference is probably due to the release of water entrapped in the crystals. In addition, the analysis time is only 1-2 min, due to the immediate availability of the water. This shorter analysis time reduces the influence of a possible change of the drift during the analysis. So, it can be assumed that the proposed method fully extracts the water content of inulin samples and can be transposed to various food ingredients presenting dissolution problems in the VKFT working medium.

Keywords: inulin, volumetric Karl Fischer titration, water content.